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ON THE ULTRA-VIOLET ABSORPTION OF THE DYESTUFFS IN SOLUTION AND THE INFLUENCE OF NEUTRAL SALTS ON THE SAME

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ABSTRACT. The paper deals with the ultra-violet absorption of a large number of fluorescent dyestuff solvents, namely, succinyl eosin, pinakryptol yellow in glycerine, acriflavine in alcohol, pinaflavol in alcohol, aniline orange in alcohol, 'rose Bengal' in alcohol, pinakryptol green in alcohol, succinyl fluorescein in glycerine. The absorption curves for each of these dyestuff are given. The effect of quenching element, namely, potassium iodide, has also been studied for acriflavine, succinyl fluorescein and pinakryptol yellow. With this particular type of quenching element it has been found that practically there is no change in the nature of absorption curves.

INTRODUCTION

A large amount of experimental work has been done by the different workers on the absorption of the dyestuff in different solvents. The existing literature on the subject reveals that the great majority of the investigators in that particular domain confined their investigations in the visible region of the spectrum. Very few quantitative measurements have been made in the ultra-violet region of the spectrum. It is well known that a quantitative measurement of absorption spectra of solutions of pure compounds can be made relatively easily, and it not only furnishes a method of identification of the substances but also serves as a basis of a theoretical treatment of their molecular structure, as is evident from the recent investigations of Mayneord,[1] Fisher[2] and others.

Mitra[3] and Grisebach[4] measured the absorption coefficient of a few dyestuffs in solution in the ultra-violet region and tried to establish a relation between the absorption curves in the near ultra-violet and polarisation curves of the fluorescent radiations emitted by these dyestuffs in solution under the excitation of light of various wave-lengths. In view of the meagre accurate data on the ultra-violet absorption, as well as, to find out whether there is any resemblance between the two sets of curves, as was reported by Grisebach and Mitra, it was thought desirable to make a systematic observation on the ultra-violet absorption of a large number of fluorescent dyestuffs in solutions.

EXPERIMENTAL ARRANGEMENTS

The absorption coefficients were determined by a calibrated rotating sector photometer (Adam Hilger) used in conjunction with a quartz spectrograph. The

source of light for the quantitative measurements has normally been a condensed tungsten-steel spark, about 4 mm. gap, the necessary potential being obtained from an X-ray induction coil with mercury interrupter in the primary. The results were in a few cases verified by the measurements of the absorption with a sensitive Moll thermopile and a galvanometer system.

A paralliel beam of light from a point source of quartz mercury lamp was allowed to fall on a cell containing the dyestuff in solution through a suitable filter, which allowed only monochromatic radiation to pass. The intensities of the incident and transmitted light were measured with the help of a Moll thermopile and galvanometer. The absorption coefficients were measured from the well-known relation :—

$$I = I_0 e^{-\alpha d},$$

where I and I_0 are the transmitted and incident intensity, respectively, of light, d, thickness of the cell containing the solution and α, the absorption coefficient.

The results of our observations in the case of both the experimental arrangements, thermoelectric and photographic, are given below for a comparative study. It will be evident that the agreement is fairly satisfactory.

TABLE I

Dyestuffs in alcoholic soln	Absorption coefficient for λ 4358 A	
	Thermoelectric	Photographic
Succ. fluorescein	.42₂	.40
Pinakryptol	.29₅	.30
Aniline orange	.24₈	.25
Pinaflavol	.44₇	.45

RESULTS

We have investigated the absorption of the following flourescent dyestuffs in alcoholic and glycerine solutions. The figures within brackets indicate the concentrations.

1. Succinyl fluorescein ... ... (1.120000)
2. Succinyl eosin ... ... (1.70000)
3. Pinaflavol ... ... (1.200000)
4. Aniline orange ... ... (1.50000)
5. Acriflavine ... ... (1.50000)
6. Pinakryptol yellow ... ... (1.100000)
7. Pinakryptol green ... ... (1·125000)
8. Rose Bengal ... ... (1.100000)

All the above compounds were purified in the usual way. The results are shown graphically by the following curves (Figs. 1 to 8). As regards the resemblance between the two sets of curves, *viz.*, absorption and polarisation curves, as already reported in our introduction, we shall return to this point in another communication.

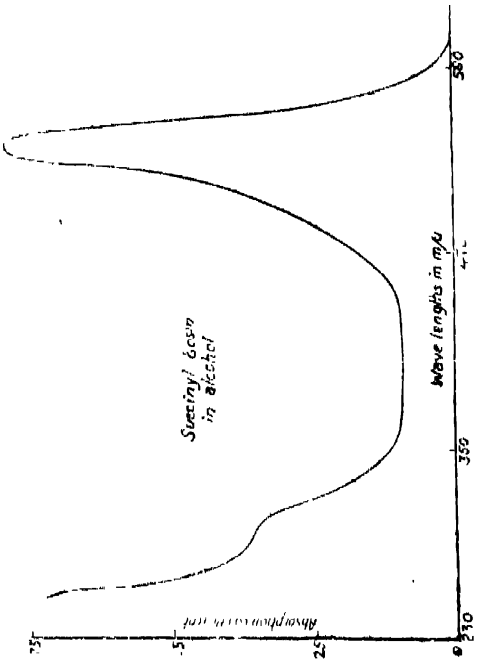

FIG. 1

FIG. 2

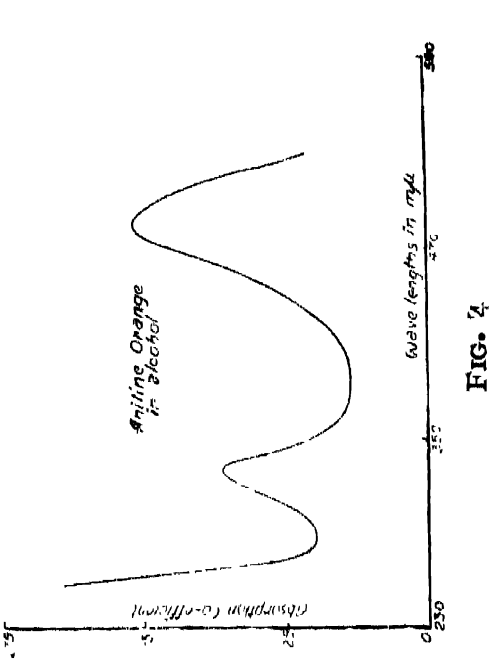

FIG. 4

FIG. 3

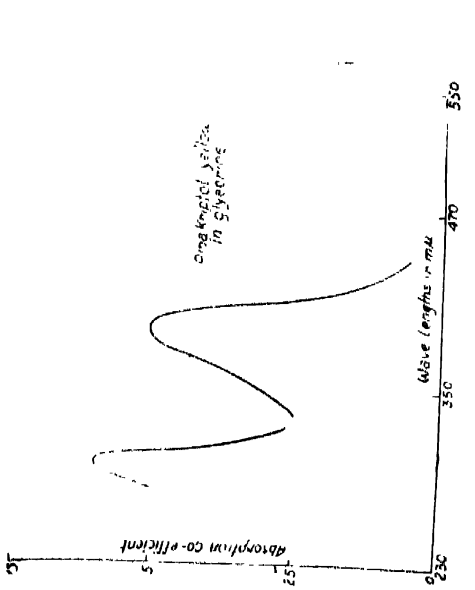

FIG. 6

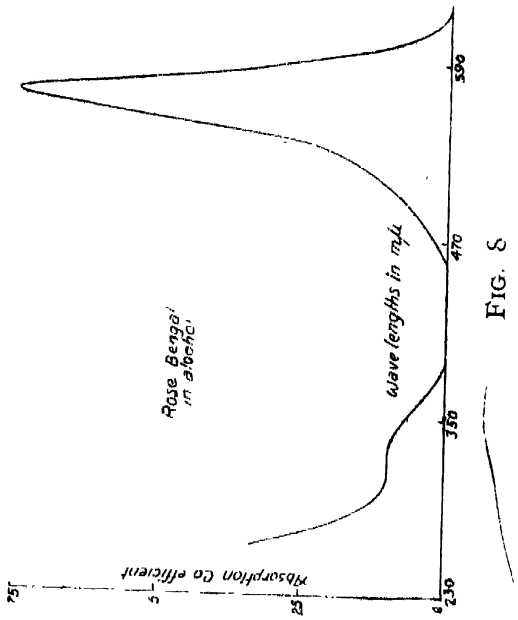

FIG. 8

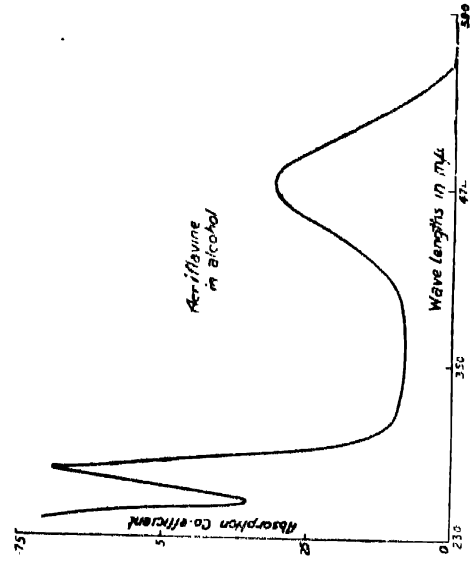

FIG. 5

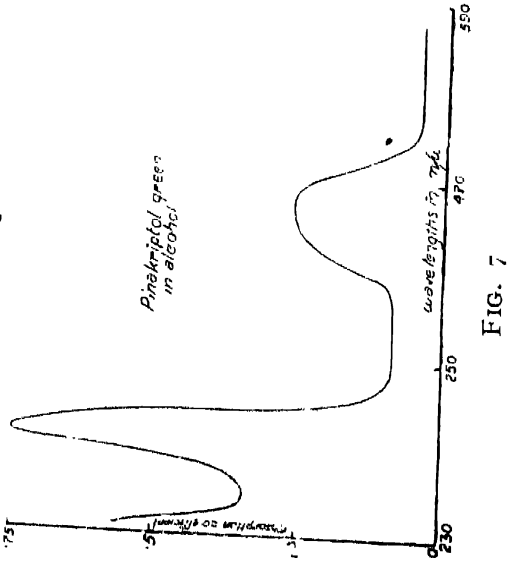

FIG. 7

INFLUENCE OF FOREIGN NEUTRAL SALTS ON THE ABSORPTION OF THE DYESTUFFS IN SOLUTION

The quenching of the flourescence of the dyestuffs in solution by foreign neutral salts is quite well known and has been investigated by a large number of workers. It appears that the majority of them are of the opinion that the phenomena of quenching are due to de-activating collisions of the second kind between the dyestuff molecules in the excited state and the negative ions of the added salts. The main argument in favour of the physical interpretation of the quenching effect is the increase of polarisation of the fluorescent radiation emitted by the dyestuffs in solutions, as was observed by Perrin,[5] Franck,[6] Mitra,[7] and

others. But there may be an alternative explanation, *viz.*,—gradual "complex formation" due to the association of the molecules of the dyestuffs and those of the quencher with the gradual addition of the foreign substance—these complex molecules being non-fluorescent. These molecules, if any, will reveal their presence by a change (or by a new band) in the absorption spectrum of the dyestuff in presence of the quencher. So, unless one studies the influence of the foreign neutral salts on the absorption of the dyestuffs and demonstrates the absence of any such influence, the aforesaid alternative explanation, *viz.*,—gradual complex molecular formation, and consequent decrease in the number of emitting dyestuffs molecules, which is exhibited by a decrease in intensity of the flourescent radiation, cannot be ruled out of the field.

The idea of complex molecular formation is not new. It is well known that as the concentration of the fluorescent substance is increased, the intensity of the fluorescent radiation also increases up to a maximum value, then the intensity falls down on further increase of the concentration of the fluorescent substance. That is, there is a definite concentration for a dyestuff for which the intensity of the fluorescent radiation is maximum. When the concentration is further increased, the resulting intensity of the fluorescent light dwindles down. In order to explain this concentration-quenching, Lewschin[8] assumed the formation of complex molecules which are non-fluorescent unlike the mother molecules. In support of his assumption he showed that when the concentration of fluorescent dyestuffs is increased over that aforesaid maximum value, considerable alteration of the absorption spectrum of the dyestuff takes place.

One finds that Lampert,[9] and Mitra[10] measured the absorption co-efficient of a few dyestuffs in solution for both pure and after the addition of varying amounts of neutral salts. Besides these, no systematic investigations have been made on the subject so far. In view of the importance of the subject on the mechanism of quenching, we thought it prudent to investigate this point along with our absorption measurements.

It has already been mentioned that the intensity of the fluorescent radiation of the dyestuffs in solution suffers appreciable diminution when neutral salts are added to the solvent medium. The investigations of Perrin,[11] West, Jetty and Muller[12] indicate that the order of the extinguishing power of the different ions is as follows :—

$$I' > CNS' > Br' > Ce' > SO_4'' > NO_3'$$

which is practically the order of their deformability, that is, of the ease of displacement of an electron in the peripheral shell of the ion. This shows that iodide ions exert the greatest quenching influence on the fluorescing dyestuff molecules. In view of this, we have investigated at present the influence of KI on the absorption of a few dyestuffs in solution.

Our experimental procedure was as follows. A solution of the dyestuff, in alcohol of requisite concentration, was taken and its absorption at different wave-lengths was determined in the usual way by the rotating sector photometer.

Then to the same solution of the dyestuff, potassium iodide solution of known concentration was added drop by drop, till the fluorescence was quenched completely, as observed visually, the concentration, c of KI being determined from the number of drops added.

Then one cell of the photometer was filled up with the quenched dyestuff solution and the other cell with the KI solution of concentration c.

For the present, we have investigated the influence of iodide ions on succ. fluorescein, succ. eosin, acriflavine and pinakryptol yellow. The results are shown graphically by the accompanying curves (Figs. 9-11).

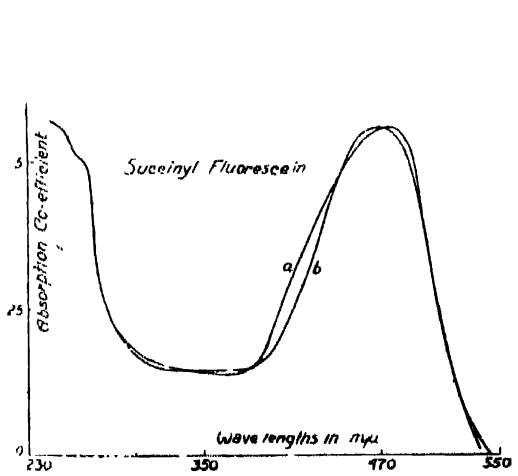

FIG. 9

Acriflavin
a—without KI
b—with KI

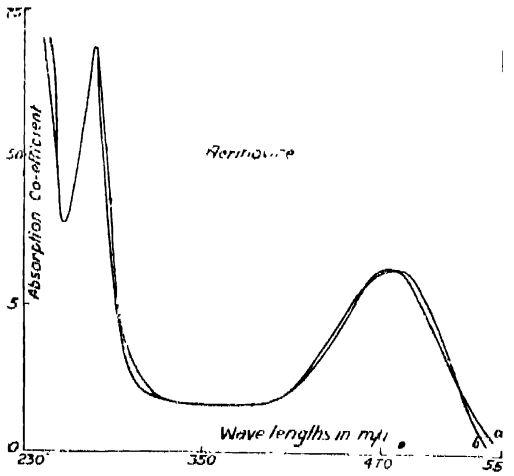

FIG. 10

Succ. flurescein
a—without KI
b—with KI

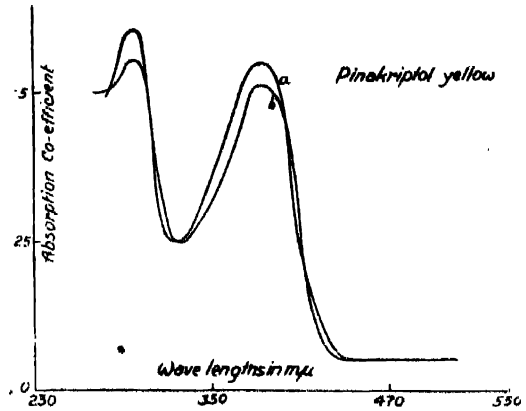

FIG. 11

Pina Kryptol yellow
a—without KI
b—with KI

The graphs show that there is practically no change in the nature of the absorption curves on the addition of the foreign neutral salt. This shows that quenching of the flourescent radiation on the addition of foreign salts takes place through collision of the second kind between the dyestuff molecules and the ions of the added salts.

In conclusion, it gives us great pleasure to thank Prof. S. N. Bose for his kind interest and Dr. S. M. Mitra for his kind guidance throughout the work.

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